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Solvothermal Synthesis and Structural Characterization of a New One-Dimensional Metal-Organic Framework $[Co(Atibdc)(Dpa)]_n$ (H_2Tibdc = 5-Amino-2,4,6-Triiodoisophthalic Acid, Dpa = 2,2'-Dipyridylamine)[1]

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Abstract—The title cobalt(II) coordination polymer, $[Co(Atibdc)(Dpa)]_n$ (**I**) ($H_2Atibdc$ = 5-amino-2,4,6-triiodoisophthalic acid, Dpa = 2,2'-dipyridylanine), has been synthesized under solvothermal conditions and characterized by elemental analysis, IR, and X-ray crystallography structural analysis. Complex **I** exhibits a one-dimensional chain structure in which 5-amino-2,4,6-triiodoisophthalate as a bridging ligand interconnects adjacent two Co(II) centers to form a helical chain structure. The asymmetric unit includes one Co(II) center, one atibdc ligand, and one Dpa ligand. Each Co(II) center is five-coordinated and surrounded by two nitrogen atoms and three oxygen atoms from one Dpa ligand and two individual Atibdc ligands, leading to distorted trigonal bipyramid geometry. Adjacent chains are further linked through hydrogen bonds, C—H—π and π—π stacking interactions to form a three-dimensional supramolecular framework.

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INTRODUCTION

During the past decade, the rational design and synthesis of coordination polymers have sparked a worldwide interest in the field of coordination chemistry and supramolecular chemistry, not only because of their intriguing topological structures but also owing to their potential applications as functional materials in asymmetric heterogeneous catalysis, magnetism, ion exchange, gas absorption, etc. [1–6]. Molecular self-assembly as an attractive approach to the fabrication of new coordination polymers has emerged, the process is spontaneously generated from their component molecular building blocks in solution [7, 8]. Although, many single-, double- and triple-helical or zigzag chains metal-organic frameworks have been generated by self-assembly processes [9–11]. However, it is still a great challenge to rational design and synthesis of the one-dimensional chain structures what we desired through a self-assembly process due to sensitive dependence on the surrounding environmental parameters, such as coordination preference of metal ions, solvent polarity, crystallization conditions and so on [12, 13]. Among them, 5-amino-2,4,6-triiodoisophthalic acid ($H_2Atibdc$) is an important ligand for translation metal complexes to generate helical or zigzag structures owing to its versatile coordination modes. In order to design and synthesis of coordination polymers with one dimensional helical or zigzag chain structures, we choose the chelating ligand 2,2'-dipyridylamine (Dpa) as a second ligand, and a new coordination polymer $[Co(Atibdc)(Dpa)]_n$ (**I**) has been successfully synthesized.

EXPERIMENTAL

Materials and methods. All reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were obtained from KBr pellets in the 4000–400 cm^{-1} range on a Nicolet 5DX spectrometer.

Solvothermal synthesis. A reaction mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.058 g, 0.2 mmol), $H_2Atibdc$ (0.056 g, 0.1 mmol), Dpa (0.034 g, 0.2 mmol), and $DMF/EtOH/H_2O$ (v/v/v = 5 : 2 : 1, 8 mL) was added to a 23 mL Teflon-lined stainless steel autoclave, which was stirred at room temperature until the mixture became homogeneous. Then it was sealed and heated at 363 K for three days, followed by slow cooling to room temperature at a rate of 5 K h^{-1}. The resulting light purple block crystals of **I** were recovered by filtration, washed with distilled water and dried at ambient temperature (57% yield, based on $Co(NO_3)_2 \cdot$

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Table 1. Crystallographic parameters and summary of data collection for structure **I**

Parameter	Value
Formula weight	786.94
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions:	
a, Å	11.102(9)
b, Å	15.440(13)
c, Å	13.376(11)
β, deg	91.38
V, Å^3	2292(3)
Z	4
ρ_{calcd}, mg cm^{-3}	2.280
Absorption coefficient, mm^{-1}	4.820
F(000)	1460
Crystal size, nm	0.37 × 0.28 × 0.20
θ Range, deg	2.01 to 26.00
Index ranges	$-13 \le h \le 13$, $-19 \le k \le 19$, $-16 \le l \le 16$
Reflections collected	23070
Independent reflections (R_{int})	4508 (0.1689)
Reflections with $I > 2\sigma(I)$	3843
T, K	293(2)
Parameters	272
GOOF	1.069
Final R indices ($I > 2\sigma(I)$)*	$R_1 = 0.0413$ $wR_2 = 0.1009$
R indices (all data)	$R_1 = 0.0480$, $wR_2 = 0.1053$
Largest diff. peak and hole, e/Å^3	1.103 and −1.298

* $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

$6H_2O$). **I** is insoluble in water and common organic solvents, such as methanol, ethanol, DMF and DMA.

For $C_{18}H_{11}N_4O_4I_3Co$

anal. calcd, %:	C, 27.47;	N, 7.12;	H, 1.41.
Found, %:	C, 27.50;	N, 7.11;	H, 1.43.

IR (ν, cm^{-1}): 3410 w, 3322 w, 1652 m, 1586 v.s, 1531 m, 1432 m, 1422 m, 1478 v.s, 1338 s, 770 s, 491m.

X-ray crystallography. Crystallographic data of **I** were collected at 293(2) K temperature on a Bruker Apex-II diffractometer with MoK_α radiation (λ = 0.71073 Å) and graphite monochromator using the ω scan mode. The structure was solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL [14–16]. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. Crystallographic data and experimental details for structural analysis are summarized in Table 1. Selected bonds lengths and bonds angles are listed in Table 2. Hydrogen bonding geometric data is listed in Table 3. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 797493; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

As shown in Fig. 1 and Table 2, each Co(II) center is five-coordinated with a distorted ZnN_2O_3 trigonal bipyramid coordination geometry consisting of three carboxylate O atoms (O(1),O(2),O(3*A*)) from two individual atibdc ligands and two N atoms (N(1) and N(3)) from one chelating Dpa ligand. The Dpa ligands coordinate in a bidentate chelating manner to link the Co^{2+} ion through the μ_2-dipyridylanine-κ^2N(1):κ^2N(3) groups, while the Atibdc ligands adopts monodentate

Table 2. Selected bond distances and angles for **I***

Bond	d, Å	Bond	d, Å
Co(1)–O(1)	2.011 (4)	Co(1)–N(1)	2.037(4)
Co(1)–O(2)	2.444 (5)	Co(1)–N(3)	2.030(4)
Co(1)–O(3)$^{\#1}$	1.977 (4)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(3)$^{\#1}$Co(1)O(1)	107.94 (15)	N(3)Co(1)N(1)	92.20(17)
O(3)$^{\#1}$Co(1)N(3)	121.16 (16)	O(3)$^{\#1}$Co(1)O(2)	90.11(14)
O(1)Co(1)N(3)	121.90(16)	O(1)Co(1)O(2)	58.03(13)
O(3)$^{\#1}$Co(1)N(1)	112.30 (16)	N(3)Co(1)O(2)	91.17(15)
O(1)Co(1)N(1)	96.44(16)	N(1)Co(1)O(2)	151.13(14)

* Symmetry codes: $^{\#1}x - 1/2, -y - 1/2, z - 1/2$.

Table 3. Intermolecular weak interactions and hydrogen bonds of **I**

Contect D–H···A	Distance, Å			Angle, deg D–H···A	Symmetry operations for A
	D–H	H···A	D···A		
N(2)–H(2*A*)···O(4)	0.86	1.96	2.811(3)	172	$-x + 1, -y - 1, -z + 2$
N(4)–H(4*A*)···I(2)	0.86	2.71	3.192(6)	117	x, y, z
N(4)–H(4*B*)···I(1)	0.86	2.76	3.229(6)	116	x, y, z
C(18)–H(18*A*)···O(2)	0.93	2.37	3.067	132	x, y, z

and bidentate bridging coordination mode to link two Co^{2+} ions through μ_1-carboxylato-κ^2 O(1)O(2) and O(3*A*) groups, with a Co···Co distance of 8.915(5) Å is linked by the structural motif to form an infinite 1D helical chain (Fig. 2). In the M–Atibdc–L system, the similar complexes [Zn(Atibdc)(4,4'-bipyridine) · $3H_2O$] [17] and [Co(Atibdc)$(Py)_3(H_2O)$ · Py] [18] have been previously reported. However, to the best of our knowledge, the feature of **I** possesses a helical chain has not been reported previously. Weak π–π stacking is observed between the pyridine ring of the Dpa ligand and benzene rings of the Atibdc ligand with a perpendicular separation of 3.609(2) Å [19], a centroid-to-centroid distance of 4.883(5) Å and a slip angle (the angle between the centroid vector normal to the plane) of 40.40°. These values are typical for π–π stacking interactions [20]. There also exist C–H–π interactions between the C(11) atom and Atribdc aromatic ring (C(2) to C(7)) at $-1/2 - x$, $1/2 - y$, $1/2 + z$, the separation of atom–ring centroid distance ~3.566(8) Å [21]. Furthermore, adjacent chains are connected together through hydrogen bonding interactions between nitrogen atoms of Dpa ligands, oxygen atoms and **I** atoms of Atibdc ligands (Table 3). The hydrogen bonding interactions, C–H–π and π–π stacking interactions link the adjacent helical chains to form 3D supramolecular framework (Fig. 3). The hydrogen bonding, π–π and C–H–π stacking interactions enhance the stability of the complex.

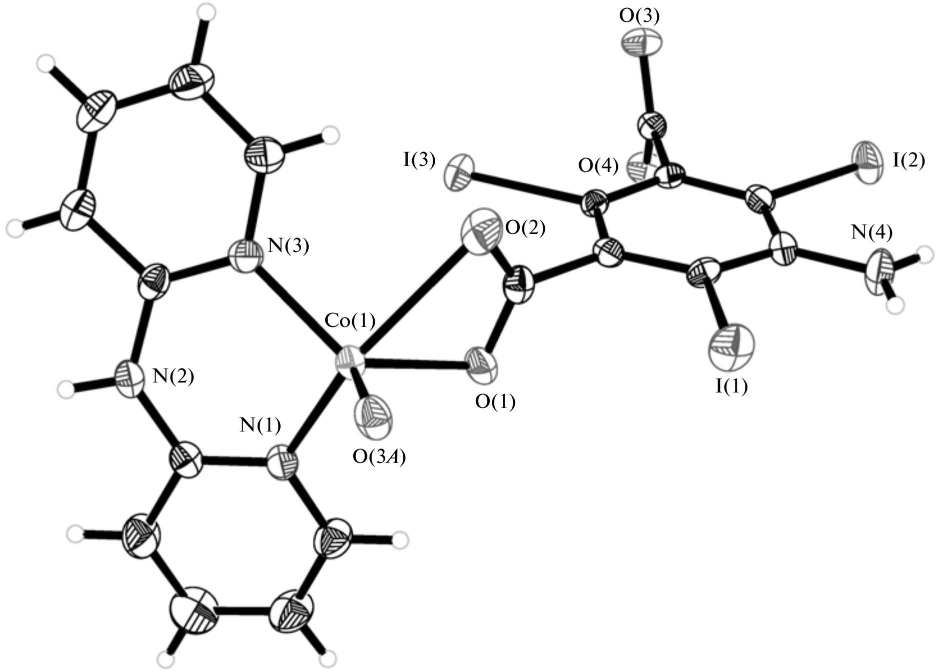

Fig. 1. Coordination environment of the Co center in **I**.

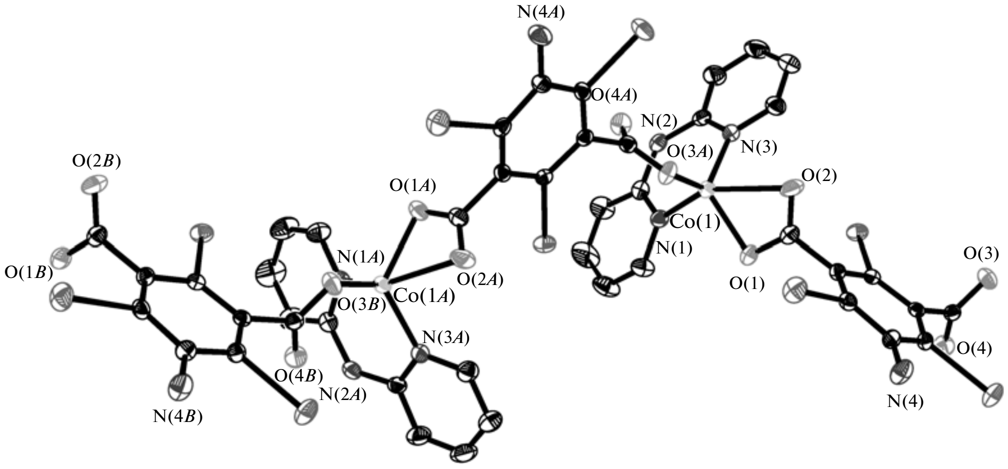

Fig. 2. Fragment of helical 1D chain structure in **I**. The hydrogen atoms are omitted for clarity.

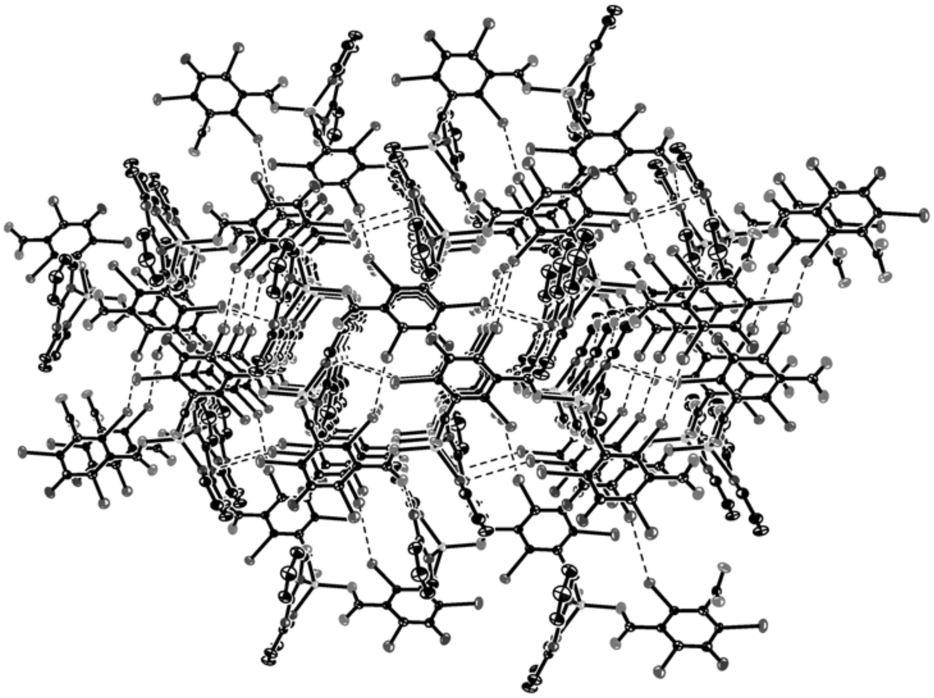

Fig. 3. The 3D framework of **I** viewed along the *x* axis.

IR spectrum of **I** not only shows that the characteristic bands of amino-groups at 3410 cm^{-1} for the asymmetric stretching and at 3320 cm^{-1} for symmetric stretching, but also illustrates that the characteristic bands of carboxyl groups at 1652, 1586 cm^{-1} for the asymmetric stretching and at 1478, 1432, 1422 cm^{-1} for symmetric stretching. The abscence of strong characteristic peaks around 1700 cm^{-1} reveals that all carboxylic groups are completely deprotonated [22–24], which is consistent with the results of the X-ray analysis.

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